Potentiometric Determination of Dissociation Constants of Dithiodiglycolic Acid in Aqueous and Aqua-Organic Media at Different Temperature and Ionic Strengths.

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Summary: The pK_{a1} and pK_{a2} values relating to the dissociation of Dithiodiglycolic acid have been determined at different temperatures 20°, 30° and 40°C and ionic strengths 0.1, 0.2, 0.5 and 1.0 M KNO_3 in aqueous media and also in aqua-organic solvents, viz. DMSO, DMF, acetonitrile, isopropanol, ethanol and methanol by employing Albert Serjeant method as refined by Noyes and Irving Rosotti method. From the variation of pK_{a1} and pK_{a2} with temperature, the values of free energy, enthalpy and entropy of dissociation are also evaluated and discussed.

Introduction

Dithiodiglycolic acid (abbreviated as DTDGA) belongs to an important class of mercapto compounds which have useful applications in biochemistry, pharmacy and in coordination chemistry.

A perusal of literature reveals some significant references on the analytical determination and separation of thioglycolic acid and dithiodiglycolic acid and their metal complexes. Mclean, Mesan et al [1], R.I. Sivkova [2] and R. Nutiu [3] reported the determination and separation of thioglycolic acid and dithiodiglycolic acids in minerals and in mixtures. C.L. Sharma and A.K. Singh [4] studied some metal complexes of dithiodiglycolic acid and its uses as a new analytical reagent for amperometric determination of cerium (IV), iron (III) and mercury (II).

However, very few references could be traced on the dissociation constants of DTDGA under different experimental conditions. K. Suzuki et al. [5] have reported the pK_{a1} and pK_{a2} values of DTDGA at 25°C and 0.1M ionic strength in aqueous medium.

In view of the scanty and inadequate literature on the subject, it was considered worthwhile to make detailed investigations on the dissociation constants of DTDGA under different experimental conditions and hence the present investigation has been undertaken.

In this communication, the pK_{a1} and pK_{a2} values relating to the dissociation of DTDGA have been determined in aqueous and aqua-organic solvents viz. 30% v/v DMSO, DMF, acetonitrile, isopropanol, ethanol and methanol; at different ionic strengths 0.1, 0.2, 0.5 and 1.0 M KNO_3 and temperatures 20°, 30° and 40°C by

employing (i) Albert Serjeant method [6] as refined by Noyes [7] (ii) Irving Rosotti method [8].

From the variation of pK_{a1} and pK_{a2} with temperature, the values of free energy, enthalpy and entropy of dissociation are also evaluated and discussed.

The knowledge of dissociation constants of mercapto acids is useful for understanding the chemistry of such compounds for two main reasons; (i) many important reactions of mercaptans may proceed through the mercaptide ions (ii) the acid dissociation constants can give important information about the distribution of electrons in mercaptans. Further, these values are involved in the study of complexation reactions of such compounds with metals.

Experimental

Dithiodiglycolic acid (DTDGA) of 100% purity was supplied by Evan's chemetics Inc. New York and all other chemicals used were of AnalaR grade. pH measurements were made on Toshniwal digital pH meter (accuracy ± 0.01 pH) with combined glass–calomel electrode assembly. The temperature of the titration cell was maintained by thermostat.

Albert Serjeant method as refined by Noyes

For determining the pK_{a1} and pK_{a2} values corresponding to the dissociation constants of Dithiodiglycolic acid having two acidic ionizing groups, the method of Albert Serjeant has been employed which involves the titration of known volume of standard DTDGA solution sequentially with two equiva-lents of standard alkali at specific temperature and ionic strenght. The pH is recorded after each addition of the titrant by means of glass electrode as soon as equilibrium is reached.

However, if it is indicated by the titration that two ionizing groups are separated by less than 2.7 units of pK_a, the usual calcuations can only give results of poor precision [6]. The end point of first equivalent is unsharp because the titration of one group begins before that of other is completed. Hence accurate results can be obtained applying Noyes modification [7].

Irving Rosotti method

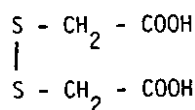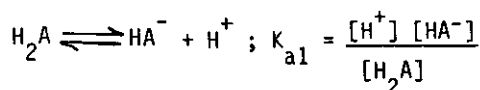The pH metric titration of the following solutions:

(a) 4mM $HClO_4$

(b) 4mM $HClO_4$ + 4mM DTDGA

against 0.2 M NaOH used as titrant were carried out at different temperatures 20°, 30°, and 40°C, varying ionic strengths 0.1, 0.2, 0.5 and 1.0 MKNO_3 and in aqua-organic solvents viz. 30% DMSO, DMF, acetonitrile, isopropanol, ethanol and methanol.
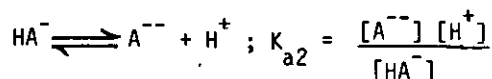
From the pH titration curves, $\bar{n}_A$ values were obtained. The pK_{a1} and pK_{a2} were obtained from pH values at $\bar{n}_A$ corresponding to 0.5 and 1.5 respectively.

Dithiodiglycolic acid (H_2A) has two replaceble hydrogen ions.

$$S - CH_2 - COOH$$
$$|$$
$$S - CH_2 - COOH$$

$$H_2A \rightleftharpoons HA^- + H^+ \; ; \; K_{a1} = \frac{[H^+][HA^-]}{[H_2A]}$$

$$pK_{a1} = pH + \log[H_2A] - \log[HA^-] \;...(1)$$

$$HA^- \rightleftharpoons A^{--} + H^+ \; ; \; K_{a2} = \frac{[A^{--}][H^+]}{[HA^-]}$$

$$pK_{a2} = pH + \log[HA^-] - \log[A^{--}] \;....(2)$$

pK_{a1} and pK_{a2} represent two acid dissociation constants whose values are determined at different temperatures,

ionic strengths in aqueous media and in different solvent-water mixtures and are recorded in Table 1.

Results and Discussion

Effect of temperature and ionic strengths

It may be seen from Table 1 that the values of pK_{a1} and pK_{a2} increase with rise in temperature indicating an increase in the degree of ionization.

However, with increase in ionic strength of the solution, these values

Table-1: Values of pK_{a1} and pK_{a2} in aqueous media at various temperature and ionic strengths.

pK	Temperature (μ= 0.1 M)			
pK	20°C	30°C	40°C	Method
	2.80	2.85	2.90	A
pK_{a1}	2.84(2.80)	2.88(2.86)	2.91(2.90)	B
	3.90	3.95	4.00	A
pK_{a2}	4.12 (3.89)	4.15(3.94)	4.18(4.00)	B
pK	Ionic strengths (temp - 30°C)			
pK	0.1	0.2	0.5	1.0M
pk_{a1}	2.85	2.83	2.8	2.70	A
	2.88(2.86)	2.85(2.82)	2.83(2.80)	2.71(2.69)	B
	3.95	3.93	3.85	3.80	A
pK_{a2}	4.15(3.94)	4.12(3.92)	4.03(3.83)	3.88(3.79)	B

A - Irving Rosotti method
B - Albert-Serjeant method
pK values in parenthesis are based on Noyes modification.

show a gradual decreasing tendency which is in accordance with the Debye Huckel equation [9] in the form

$$pK = pK_0 - [A / \bar{\mu} (1 + / \bar{\mu})^-] + Cu$$

Effects of solvents

The determination of dissociation constants [10,11] in solvent water mixtures necessitates the accurate estimation of H^+ ion concentration in the mixed media. The pH meter reading obtained in different solvent-water media, does not give the correct H^+ ion activity on account of several factors arising from (a) liquid-junction potentials of uncertain magnitude (b) changes in the sensitivity of the glass electrode and (c) solute-solvent interactions.

Table-2: Values of pK_{a1} and pK_{a2} in 30% (v/v) aqua-organic media at 30°C ($\mu = 0.1M$)

Solvent	pK_{a1}	pK_{a2}
DMSO	3.30	4.34
DMF	3.20	4.25
Acetonitrile	3.10	4.15
Isopropanol	3.08	4.12
Ethanol	3.05	4.08
Metahnol	3.00	4.04

Hence appropriate correction was applied to the pH meter reading in different solvents as suggested by Van Uitert [12] to get the true hydrogen ion concentration.

For the same v/v composition pK_{a1} and pK_{a2} in different solvent water mixture follow the order.

DMSO-water > DMF-water > acetonitrile -water > isopropanol-water > ethanol-water > methanol-water

which may be explained on the basis of change in dielectric constant [13] of the medium ion pair formation, ionic interaction proton-solvation and viscosity [14].

Thermodynamic parameters

From the variation of pK_{a1} and pK_{a2} with temperature, values of ΔG, ΔH and ΔS were determined at 30°C ($\mu = 0.1M$) by applying the usual thermodynamic relations [15] and are recorded as under:

pK	ΔG (kcl/mole)	ΔH (kcl/mole)	ΔS (cal/deg/mole)
pK_{a1}	3.95	2.09	-6.13
pK_{a2}	5.41	2.20	-10.75

The positive values of G indicate that under standard state conditions, the dissociation reaction is endergonic, i.e., which utilizes (requires) energy. It is established [16] that in case pK_a increase with increasing temperature, ΔH is positive and if it decreases with increasing temperature ΔH is negative. The increasing pK_a values with temperature (Table 1) support the positive value of ΔH; besides it also reveals the endergonic (endothermic) nature of the reaction. The negative values of ΔS account for charge separation during dissociation.

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